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Identification of Polybrominated Biphenyls in the Adipose Tissues of the General Population of the United States

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16. ABSTRACT

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Identification of Polybrominated Biphenyls in the Adipose Tissues of the General Population of the United States

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Abstract

Hexabromobiphenyl has been identified by gas chromatography/mass spectrometry (GC/MS) in pooled extracts of adipose tissue samples collected from the general population of the conterminous United States. Mass spectra derived from tissue extracts subjected to gel permeation chromatography were compared with those obtained from an authentic PBB mixture containing 2,4,5,2′,4′,5′-hexabromobiphenyl as the principal component. GC retention times and unique characteristics of the mass spectrum permitted confirmation of identity of the hexabromo isomer. Levels in one tissue sample were determined to be in the 1 to 2 ppb range.

Introduction

Polybrominated biphenyls (PBBs) have been reported in the blood (1) and adipose tissues (2) of Michigan chemical workers and residents who were exposed directly or indirectly in 1973-74 to the fire retardant fireMaster® BP-6. The principal ingredient of the commercial product has been shown to be 2,4,5,2′,4′,5′-hexabromobiphenyl, making up about 56% of the total mixture (3,4). The remainder of the mixture consists primarily of other hexabromobiphenyl isomers and penta- and heptabromobiphenyls (3). As a result of the Michigan episode, this laboratory began a search for evidence of PBB contamination in the general population of the United States. Examination of pooled extracts of human adipose tissue specimens collected under the National Human Monitoring Program operated by the U.S. Environmental Protection Agency (5) has revealed the presence of hexabromobiphenyls in nearly all such samples examined during the last several years.

Experimental

Materials and Standards

All solvents were distilled-in-glass (Burdick and Jackson, Muskegon, Michigan) or equivalent. An authentic standard of fireMaster® BP-6 hexabromobiphenyl, Lot No. 06151, was obtained from Michigan Chemical Corporation (Chicago, Illinois).

Samples

Composite samples of human adipose tissue extracts were obtained directly from laboratories participating in the National Human Monitoring Program. These samples represented the pooled extracts of several hundred individual tissue samples collected in a statistically valid manner from all nine census regions of the conterminous United States. Each sample had been subjected to a modified Mills-Onley-Gaither cleanup procedure (6). The 6% diethyl ether in hexane fractions from Florisil chromatography of the individual samples were concentrated and pooled. The pooled extracts were subjected to gel permeation chromatography (GPC) in this laboratory according to the procedure of MacLeod *et al.* (7). The GPC eluant was concentrated to 50 μL at room temperature under a gentle stream of nitrogen for GC/MS analysis.

Gas Chromatography/Mass Spectrometry

Electron impact mass spectra were obtained on a Finnigan 4023 gas chromatography/mass spectrometry/computer system. A mass range of 390 to 800 m/z was scanned in 1.7 seconds, and the 70 eV mass spectra recorded with a filament emission of 0.40 mA and an electron multiplier voltage of 1.5 kV. A 12 m x 0.2 mm i.d. fused silica OV-101 WCOT capillary column was connected directly to the ion source and was temperature programmed from 60 °C (1 min) to 300 °C (30 min) at 8 °C/min. The carrier gas was helium at a flow of 1.5 mL/min. Typically, 4 μL of sample was injected for analysis.

Results and Discussion

Figure 1 shows a light beam oscillographic (LBO) tracing of the 450-650 m/z range of a mass spectrum obtained from the pooled extracts of samples collected during 1978. The presence of hexabromobiphenyl is clearly indicated through the $M^{\cdot+}$ six-bromine cluster, the largest member of which is centered at 627.5 m/z ($C_{12}H_4{}^{79}Br_3{}^{81}Br_3$); the $M^{\cdot+}$-Br cluster at 546.6 m/z ($C_{12}H_4{}^{79}Br_3{}^{81}Br_2$); and the $M^{\cdot+}$-2Br cluster at 467.7 m/z ($C_{12}H_4{}^{79}Br_2{}^{81}Br_2$). The relative abundance of the molecular ion,

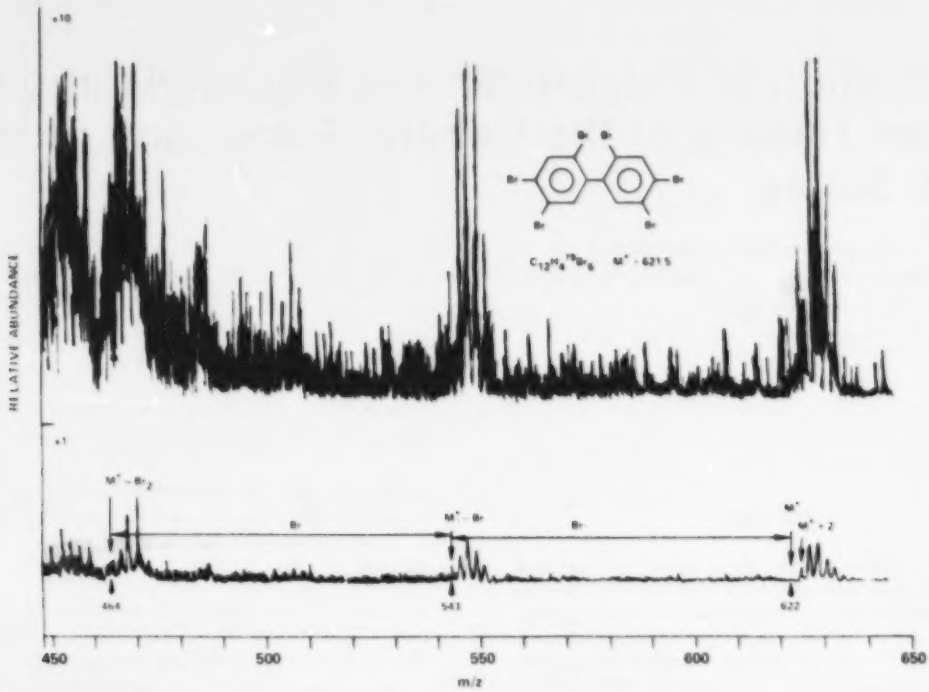

Figure 1. Light beam oscillographic tracing of mass spectrum of hexabromobiphenyl from pooled human adipose tissue extract.

621.5 m/z ($C_{12}H_4{}^{79}Br_6$), is only 5.3% that of the largest component of the six-bromine cluster. Supporting evidence for the 2,4,5,2′,4′,5′ isomer was based on the identity of the GC retention time (14.3 min) of the sample component with that of the major component of fireMaster BP-6 and on the large $M^{\cdot+}$-Br fragment attributable to an *ortho* effect of the 2,2′ bromine substitution. (8).

A computer-reconstructed mass spectrum from another composite sample collected during January to June 1981 is shown in Figure 2. Again, the 627.5 m/z molecular ion cluster of hexabromobiphenyl is apparent, but the $M^{\cdot+}$-Br and $M^{\cdot+}$-2Br ions are partially obscurred by chlorine clusters from nonachloroterphenyls (major $M^{\cdot+}$ component, 540 m/z) and heptachloroterphenyls (468 m/z). The cluster centered at 504 m/z corresponds to octachloroterphenyls. The ubiquitous occurrence of polychlorinated terphenyls (PCTs) in the adipose tissues of U.S. citizens has been previously reported (9).

The mass spectrum shown in Figure 2 was obtained from a sample of pooled tissue specimens collected from 202 individuals. The wet weights totaled about 600 g. Based on this weight, the average concentration of hexabromobiphenyl in the total sample was estimated to be 1 to 2 ng/g (ppb).

Other pooled samples in which PBBs were detected came from national collections made during the first six months of 1977, all of 1978, the last half of 1980, and the first half of 1981. It should be noted, however, that the absence of PBBs in other composite samples surveyed during the period was not confirmed since all were not analyzed specifically for these compounds. It is conceivable that the presence of PBBs in the composite samples analyzed may be due to the inclusion of one or several specimens with high PPB concentrations (upper ppb to ppm

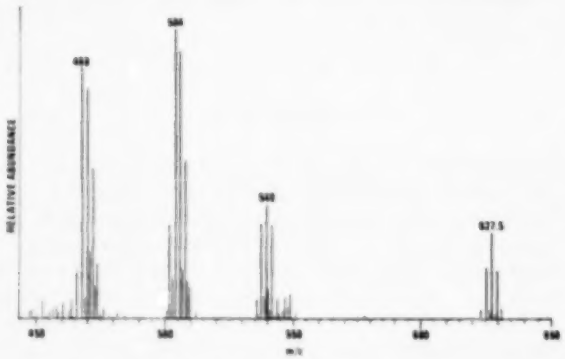

Figure 2. Mass spectrum of hexabromobiphenyls and polychlorinated terphenyls from pooled human adipose tissue extract.

levels). However, the wide spread use of these compounds as fire retardants (4) may mean that PBBs, like PCBs and PCTs, have become ubiquitous contaminants in the U.S. population.

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This paper has been reviewed by the Health Effects Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement nor recommendation for use.

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